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(54) **Water-in-oil emulsified cosmetic**

(57) The present invention is a water-in-oil emulsified cosmetic comprising

(A) a complex obtained by mixing an ampholytic surfactant or semi-polar surfactant and higher fatty acid, and

(B) an inorganic salt and/or amino acid salt, in order to provide a water-in-oil emulsified cosmetic with excellent stability over time and superior usability which allows emulsification of a large amount of water in a wide range of oils from polar oil to non-polar oil.

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Description

Related Application

5 [0001] This application claims the priority of Japanese Patent application No.11-109048 filed on April 16, 1999, which is incorporated herein by reference.

Background of the Invention

10 **1. Field of the invention**

[0002] This invention relates in general to a water-in-oil emulsified cosmetic, and more particularly to a water-in-oil emulsified cosmetic which gives moisture to the hair or the skin, is moisturizing yet not sticky, and has superior stability over time.

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2. The Prior Art

[0003] For the emulsifier of a conventional water-in-oil (W/O) emulsified cosmetic, polyhydric alcohol fatty ester-based surfactants such as glycerine fatty acid ester and sorbitan fatty acid ester as well as polyoxyalkylene-modified organopolysiloxane-based surfactants are generally used.

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[0004] However, in a W/O emulsion, separation of the oil phase, which is the continuous phase, tends to occur at lower temperatures due to aggregation of water drops. On the other hand, at higher temperatures water drops tend to merge to increase the particle size and therefore sink, leaving only the oil in the top layer, resulting in separation of the oil phase.

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[0005] Considering this problem, for the purpose of improving the temperature stability, a method in which a large amount of wax is blended in to increase the viscosity has been used. However, even with this method, the stability at higher temperatures is not sufficient.

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[0006] Also, since the outer phase of a W/O emulsion is oil, there are advantages such as skin protection and making the skin supple. On the other hand, however, there are problems in terms of usability such as stickiness at the time of use, poor spreadability, and hardness.

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[0007] Based on the situation described above, the inventors conducted earnest research to solve the aforementioned problem and discovered that a water-in-oil emulsified cosmetic which is prepared by combining a complex obtained by mixing an ampholytic surfactant or semi-polar surfactant and higher fatty acid and inorganic salt and/or amino acid salt allows stable emulsification of a large amount of water in a wide range of oils including non-polar oils such as silicone oil, triglycerides, ester oils, and hydrocarbons, as well as polar oils, and thus provides a water-in-oil emulsified cosmetic which has superior stability over time and superior usability, thus completing the present invention.

[0008] The object of the present invention is to provide a water-in-oil emulsified cosmetic which enables blending of a large amount of water, has superior stability over time as well as superior usability.

40 **Brief Summary of the Invention**

[0009] That is, the present invention provides a water-in-oil emulsified cosmetic which characteristically contains

- 45 (A) a complex obtained by mixing an ampholytic surfactant or semi-polar surfactant and higher fatty acid and
(B) an inorganic salt and/or amino acid salt.

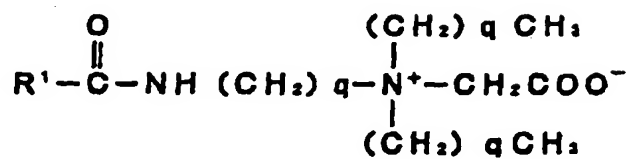
[0010] Also, the present invention provides the aforementioned water-in-oil emulsified cosmetic wherein said ampholytic surfactant or semi-polar surfactant is one or more surfactants selected from the group consisting of surfactants represented by the following general formulas (1)-(6).

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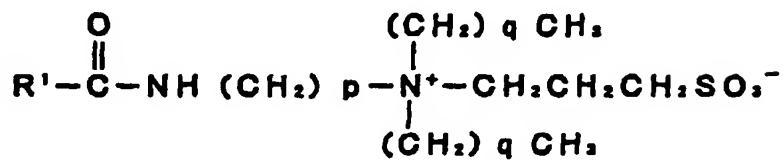
General formula (1): Amidobetaine ampholytic surfactants

[0011]



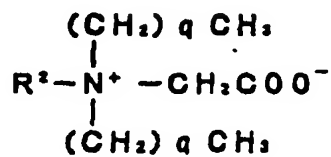
General formula (2): Amidosulfobetaine ampholytic surfactants

[0012]



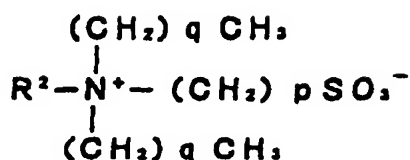
General formula (3): Betaine ampholytic surfactants

[0013]



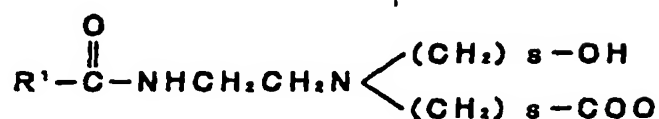
General formula (4): Sulfobetaine ampholytic surfactants

[0014]



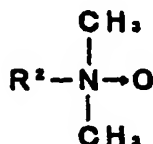
General formula (5): Imidazolinium ampholytic surfactants

[0015]



General formula (6): Tertiary amine oxide semi-polar surfactants

[0016]



[0017] [In general formulas (1)-(6), R_1 denotes an alkyl or alkenyl group having 9-21 carbon atoms, R_2 and R_3 denote alkyl or alkenyl groups having 10-18 carbon atoms. p denotes an integer 2-4, q denotes an integer 0-3, and s denotes an integer 1 or 2.]

[0018] Furthermore, the present invention provides the aforementioned water-in-oil emulsified cosmetic wherein said higher fatty acid (A) is a higher fatty acid represented by the following general formula (7).



General formula (7)

[Where R_4 denotes a linear chain, branched chain, or hydroxide-group-containing saturated or unsaturated hydrocarbon having 7-25 carbon atoms.]

[0019] Also, the present invention provides the aforementioned water-in-oil emulsified cosmetic wherein the weight ratio of (higher fatty acid) : (ampholytic surfactant or semi-polar surfactant) in said complex (A) is 0.5 : 9.5-9.5 : 0.5.

[0020] Furthermore, the present invention provides the aforementioned water-in-oil emulsified cosmetic wherein said inorganic salt (B) is one or more salts selected from the group consisting of sodium chloride, potassium chloride, magnesium chloride, calcium chloride, aluminum chloride, sodium sulfate, potassium sulfate, magnesium sulfate, and

aluminum sulfate.

[0021] Also, the present invention provides the aforementioned water-in-oil emulsified cosmetic of a high inner water phase type wherein the water content is 70.0 wt% or more of the total amount of the water-in-oil emulsified cosmetic.

Detailed Description of the Invention

[0022] The configuration of the present invention is described below.

[0023] The complex used in the present invention is obtained by mixing an ampholytic surfactant or semi-polar surfactant and higher fatty acid. The carboxyl group of the higher fatty acid is bonded to the ampholytic surfactant or semi-polar surfactant to form the complex. The details are described in Japanese unexamined patent publication Tokkai Kei 6-65596.

[0024] In the present invention, since this complex acts as an excellent emulsifier, a superior emulsified composition can be prepared without using other surfactants or emulsifiers.

[0025] For the ampholytic surfactant or semi-polar surfactant in the complex, while any ampholytic surfactant or semi-polar surfactant used as usual cosmetic base ingredients can be used, more preferable are the surfactants represented by the aforementioned general formulas (1)-(6).

[0026] In the aforementioned general formulas (1)-(6), R_1 is an alkyl group or alkenyl group having 9-21 carbon atoms, preferably an alkyl group or alkenyl group having 11-17 carbon atoms, and more preferably an alkyl group or alkenyl group having 11-13 carbon atoms. If the carbon number is less than 9, then the hydrophilicity is too strong. On the other hand, if it is more than 21, then solubility in water becomes poor. R_2 and R_3 denote alkyl groups or alkenyl group having 10-18 carbon atoms. p denotes an integer 2-4, q denotes an integer 0-3, and s denotes an integer 1 or 2.

[0027] For the surfactants of the aforementioned general formulas (1)-(6), commercially available products can be used. Specific examples of commercially available amido betaine ampholytic surfactants of general formula (1) include Lebon 2000 (from Sanyo Chemical Industries, Ltd.) and Anon BDF (from Nippon Oil and Fats Co., Ltd.).

[0028] Specific examples of commercially available amido sulfobetaine ampholytic surfactants of general formula (2) include Lonzaine (from Lonza Inc.) and Milataine (from Milanol Co., Ltd.).

[0029] Specific examples of commercially available betaine ampholytic surfactants of general formula (3) include Anon BL (from Nippon Oil and Fats Co., Ltd.) and Dehyton (from Henkel Corporation).

[0030] Specific examples of commercially available sulfobetaine ampholytic surfactants of general formula (4) include Ronzaine (from Ronza Co., Ltd.).

[0031] Specific examples of commercially available imidazolinium ampholytic surfactants of general formula (5) include Obazolin (from Toho Chemical Industry Co., Ltd.) and Anon GLM (from Nippon Oil and Fats Co., Ltd.).

[0032] Specific examples of commercially available tertiary amine oxide semi-polar surfactants of general formula (6) include Unisafe A-LM (from Nippon Oil and Fats Co., Ltd.) and Wondamine (from Shin Nihon Rika Co., Ltd.).

[0033] Any one or more of these ampholytic surfactants or semi-polar surfactant can be selected for use in the complex of the present invention.

[0034] For the higher fatty acid in the present invention, while any higher fatty acid used as usual cosmetic base ingredients can be used, more preferable are the higher fatty acids represented by the aforementioned general formula (7).

[0035] In the aforementioned general formula (7), R_4 is a linear chain, branched chain, or hydroxide-group-containing saturated or unsaturated hydrocarbon having 7-25 carbon atoms, and more preferable is a linear chain, branched chain, or hydroxide-group-containing saturated or unsaturated hydrocarbon having 11-21 carbon atoms. If the carbon number is less than 7, then the hydrophilicity is too strong and the complex is hard to form. On the other hand, if the carbon number is more than 25, then the melting point is too high and the complex is hard to form.

[0036] Specific examples of the higher fatty acid represented by the aforementioned general formula (7) include saturated fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, unsaturated fatty acids such as 2-palmitoic acid, petroselic acid, oleic acid, elaidic acid, ricinolic acid, linolic acid, linoelaidic acid, linolenic acid, and arachidonic acid, branched chain fatty acids such as isostearic acid, and hydroxycarboxylic acids such as 12-hydroxystearic acid.

[0037] In the present invention, any one or more of these higher fatty acids are selected and used.

[0038] It is preferable, in terms of stability, to adjust the blend ratio between the higher fatty acid and the ampholytic surfactant or semi-polar surfactant in the complex such that the weight ratio of the former against the latter is $0.5 : 9.5 - 9.5 : 0.5$ {(higher fatty acid)/(ampholytic surfactant or semi-polar surfactant)} = $0.05-19$, more preferably $1 : 9 - 9 : 1$ {(higher fatty acid)/(ampholytic surfactant or semi-polar surfactant)} = $0.1-9$.

[0039] The total amount of the ampholytic surfactant or semi-polar surfactant and the higher fatty acid is, in terms of stability, preferably 0.1-30.0 wt%, and more preferably 0.5-20.0 wt%.

[0040] The complex of ampholytic surfactant or semi-polar surfactant and the higher fatty acid used in the present

invention can be added to the recipe of the emulsified cosmetic after mixing the two together. However, it is also possible to blend in the ampholytic surfactant or semi-polar surfactant and the higher fatty acid along with other ingredients in the recipe.

[0041] Next, the stabilizers in the present invention, i.e. (B) the inorganic salt and/or amino acid salt, are described.

[0042] Examples of the inorganic salt used in the present invention include alkali metal salts, alkali earth metal salts, aluminum salts, zinc salts, or ammonium salts of hydrochloric acid, sulfuric acid, nitric acid, carbonic acid, phosphoric acid, and lactic acid. Preferable examples of the inorganic salt include chlorides such as sodium chloride, potassium chloride, magnesium chloride, calcium chloride, aluminum chloride, zinc chloride, and ammonium chloride, sulfates such as sodium sulfate, potassium sulfate, magnesium sulfate, aluminum sulfate, zinc sulfate, and ammonium sulfate, nitrates such as sodium nitrate, potassium nitrate, magnesium nitrate, calcium nitrate, aluminum nitrate, zinc nitrate, and ammonium nitrate, carbonates such as sodium carbonate, potassium carbonate, magnesium carbonate, and calcium carbonate, phosphates such as sodium phosphate and potassium phosphate. Particularly preferable among those are sodium chloride, potassium chloride, magnesium chloride, calcium chloride, aluminum chloride, sodium sulfate, potassium sulfate, magnesium sulfate, and aluminum sulfate.

[0043] The blend ratio of the inorganic salt used in the present invention is 0.1-8.0 wt%, preferably 0.2-5.0 wt%, of the total amount of the emulsified cosmetic. If it is less than 0.1 wt%, then the emulsion cannot be stabilized. There is no increase in the efficacy if the blend ratio increases over 8.0 wt%.

[0044] The amino acid salt used in the present invention is an amino acid whose carboxyl group or amino group forms a salt. Examples include sodium aspartate, potassium aspartate, magnesium aspartate, sodium glutamate, potassium glutamate, magnesium glutamate, calcium glutamate, glutamic acid hydrochloride, cysteine hydrochloride, histidine hydrochloride, lysine hydrochloride, ornithine hydrochloride, ornithine acetate, tryptophan hydrochloride, arginine glutamate, ornithine glutamate, lysine glutamate, lysine aspartate, and ornithine aspartate. Of these, sodium glutamate is preferable.

[0045] The blend ratio of the amino acid salt used in the present invention is 0.1-8.0 wt%, preferably 0.2-5.0 wt%, of the total amount of the emulsified cosmetic. If it is less than 0.1 wt% then the emulsion cannot be stabilized. There is no increase in the efficacy if the blend ratio increases over 8.0 wt%.

[0046] For the stabilizer of the present invention, it is sufficient to use one of the aforementioned inorganic salts or amino acid salts, but two or more inorganic salts or amino acid salts can be mixed as well. In such a case, the total blend ratio is 0.1-8.0 wt%, preferably 0.2-5.0 wt%.

[0047] Selection of the oil component used in the water-in-oil emulsified cosmetic of the present invention is not limited in particular, and oil components which are normally used in emulsified cosmetics can be used. Examples are widely varied from polar oils to non-polar oils, including fats/oils such as olive oil, coconut oil, safflower oil, castor oil and cottonseed oil, waxes such as lanolin, jojoba oil, carnauba wax, and candelilla wax, hydrocarbon oils such as liquid paraffin, squalane, and petrolatum, fatty acids, ester oils such as cetyl octanoate and isopropyl myristate, silicone oils such as dimethyl polysiloxane, methylphenyl polysiloxane, amino-modified silicone, and fluoride-modified silicone, as well as their gum-like silicone, and perfluoropoly ether.

[0048] The blend ratio of the oil component is 5.0-30.0 wt%, preferably 7.0-25.0 wt%.

[0049] The water content of the water-in-oil emulsified cosmetic of the present invention is 65.0-70.0 wt%, preferably 70.0 wt% or more, of the total amount of the water-in-oil emulsified cosmetic. For the present invention, water-in-oil emulsified cosmetics with a high inner water phase are preferable.

[0050] In addition to the aforementioned essential ingredients, other ingredients can be blended into the water-in-oil emulsified cosmetic of the present invention as necessary within the quantitative and qualitative range which does not affect the effect of the present invention, and preparation can be conducted with a conventional method. Examples of these ingredients include water soluble polyhydric alcohols such as ethylene glycol, propylene glycol, 1,3-butylene glycol, glycerine, polyglycerine, sorbitol, and polyethylene glycol, humectants such as hyaluronic acid, chondroitin sulfuric acid, and pyrrolidone carboxylate, ultraviolet light absorbers, ultraviolet light scattering agents, resins such as acrylic type resins and polyvinylpyrrolidone, proteins or hydrolyzed proteins such as soybean protein, gelatin, collagen, silk fibroin, and elastin, preservatives such as ethyl paraben and butyl paraben, various amino acids, activating agents such as biotin and pantothenic acid derivatives, blood circulation promoting agents such as gamma-oryzanol, sodium dextran sulfate, vitamin E derivatives and nicotinic acid derivatives, anti-seborrheic agents such as sulfur and thiantol, diluents such as ethanol and isopropanol, thickeners such as hydroxyethyl cellulose, pharmaceuticals, fragrance preservatives, colored pigments, bright pigments, organic powder, hydrophobically treated pigments, and tar pigments.

[0051] Examples of the water-in-oil emulsified cosmetic of the present invention include emulsions or cream products such as an emulsion, cream, foundation, eye liner, mascara, and eye shadow.

[0052] According to the present invention, a large amount of water can be emulsified in a wide range of oils including silicone oils, triglycerides, ester oils, and hydrocarbons, and a water-in-oil emulsified cosmetic with excellent stability over time and superior usability can be provided.

Examples

[0053] The present invention is described in detail by referring to examples below. The present invention is not limited to these examples. The blend ratios are indicated in weight percent units.

[Examples 1-4 and Comparative examples 1-4]

[0054] Cream, which is an emulsified cosmetic, was prepared using the recipe shown in Table 1 and the stability and usability of the obtained cream was evaluated by means of a stability test and an actual use test by a panel of ten female specialists. The stability test results were obtained by evaluating the appearance after the samples were allowed to stand for one month at 50°C, and the actual use test was conducted by evaluating the preferences during the use, each based on the following evaluation criteria, respectively.

[Evaluation criteria of the stability]

[0055]

○ : No separation was observed.

△ : Almost no separation was observed.

X : Separation of a liquid phase (oil phase or water phase) occurred.

[Evaluation criteria of the usability]

[0056]

○ : Seven or more of the ten female specialists in the panel reported the sample was glossy, moist but not sticky, and judged that the usability was good.

△ : Three or more and less than seven of the ten female specialists in the panel reported the sample was glossy, moist but not sticky, and judged that the usability was good.

X : Less than three of the ten female specialists in the panel reported the sample was glossy, moist but not sticky, and judged that the usability was good.

Table 1

	Example				Comparative example		
	1	2	3	4	1	2	3
(1) Dimethylpolysiloxane (20mPa · s)	10.0	10.0	10.0	10.0	10.0	10.0	10.0
(2) Isostearic acid [Trade name: Isostearic acid EX from Kokyu Alcohol Kogyo Co., Ltd.]	2.0	2.0	2.0	2.0	2.0	2.0	2.0
(3) Sodium 2-undecyl-N,N,N-(hydroxyethylcarboxymethyl)-2-imidazolin (net 30%) [Trade name: Obazolin 662N from Toho Chemical Industry Co., Ltd.]	5.0	5.0	5.0	5.0	5.0	5.0	5.0
(4) Ion exchanged water	77.0	77.0	77.0	77.0	77.0	77.95	63.0
(5) Ethanol	5.0	5.0	5.0	5.0	5.0	5.0	5.0
(6) Sodium glutamate	1.0	-	-	0.5	-	-	15.0
(7) Potassium chloride	-	1.0	-	-	-	-	-
(8) Sodium chloride	-	-	1.0	0.5	-	0.05	-
Stability	○	○	○	○	X	X	○
Usability	○	○	○	○	○	○	X

Preparation method)

[0057] (1) and (2) were mixed, and the water phase consisting (3), (4), and (5) in which (6) or (7) or (8) was dissolved was gradually added to the oil phase at room temperature by means of a high-speed stirrer (disper) to obtain the target W/O emulsified cosmetic cream.

[0058] As indicated in Table 1, the high inner water phase type water-in-oil emulsified cosmetic of the present invention was an excellent cosmetic which was superior in both stability and usability, and gave a fresh sensation during use.

[0059] Other examples of the present invention are listed below.

"Example 5" Skin cream	wt%
(1) Liquid paraffin	6.0
(2) Decamethylcyclopentasiloxane	10.0
(3) 1,3-butylene glycol	3.0
(4) Oleic acid	1.5
(5) Cocoyl amido propyldimethyl glycine (net 30%) [Trade name: Lebon 2000-SF, Sanyo Chemical Industries, Ltd.]	2.0
(6) Ion exchanged water	71.3
(7) Sodium glutamate	3.0
(8) Paraben	0.2
(9) Antioxidant	Appropriate amount
(10) Ethanol	3.0
(11) Perfume	Appropriate amount

Preparation method)

[0060] (1), (2), and (4) were mixed to prepare the oil phase beforehand. The water phase prepared by mixing/stirring/dissolving (3), (5), (6), (7), (9), (10), and (11) was gradually added to the oil phase at room temperature while being stirred by means of a high-speed stirrer (disper) to obtain the target skin cream.

Effect)

[0061] The same evaluation as for Examples 1-4 was conducted for the obtained skin cream. The usability was excellent (usability evaluation: ○). When applied on the skin, it gave moisture, provided a moisturizing sensation and yet was not sticky, and had good stability (stability evaluation: ○).

"Example 6" Hair treatment cream	wt%
(1) Isoparaffin	3.0
(2) Dimethylpolysiloxane (500 mPa · s)	5.0
(3) Glycerine	5.0
(4) Isostearic acid [Trade name: Emery #875 from Emery Co., Ltd.]	3.0
(5) Lauryl dimethyl aminoacetic acid betaine (net 30%) [Trade name: Anon BL from Nippon Oil and Fats Co., Ltd.]	1.0
(6) Ion exchanged water	72.9
(7) Ethanol	8.0

(continued)

"Example 6" Hair treatment cream	wt%
(8) Sodium chloride	2.0
(9) Paraben	0.1
(10) Perfume	Appropriate amount

Preparation method)

[0062] (1), (2), and (4) were mixed to prepare the oil phase beforehand. The water phase prepared by mixing/stirring/dissolving (3) and (5)-(10) was gradually added to the oil phase at room temperature while being stirred by means of a high-speed stirrer (disper) to obtain the target hair treatment cream.

Effect)

[0063] The same evaluation as for Examples 1-4 was conducted for the obtained hair treatment cream. The usability was excellent (usability evaluation: ○). When applied on the hair, it gave moisture, provided a moisturizing sensation and yet was not sticky, and had good stability (stability evaluation: ○).

"Example 7" W/O emulsified foundation	wt%
(1) Squalane	1.0
(2) Dimethylpolysiloxane (6 mPa · s)	3.0
(3) Propylene glycol	2.5
(4) Isostearic acid [Trade name: Isostearic acid PK form Kokyu Alcohol Kogyo Co., Ltd.]	2.5
(5) Sodium 2-undecyl-N,N,N-(hydroxyethylcarboxymethyl)-2-imidazoline (net 28%) [Trade name: Sofdazoline LHL-saltfree from Kawaken Fine Chemicals Co., Ltd.]	1.0
(6) Ion exchanged water	70.9
(7) Ethanol	1.0
(8) Sodium glutamate	1.5
(9) Potassium chloride	1.5
(10) Paraben	0.1
(11) Titanium dioxide treated with dextrin palmitate	5.0
(12) Mica treated with dextrin palmitate	5.0
(13) Talc treated with dextrin palmitate	2.5
(14) Iron oxide treated with dextrin palmitate	2.5
(15) Antioxidant	Appropriate amount
(16) Perfume	Appropriate amount

Preparation method)

[0064] (1), (2), (4), and (11)-(14) were mixed and dispersed to prepare the oil phase beforehand. The water phase prepared by dissolving (3), (5), (6), (7), (8), (9), (10), (15), and (16) was gradually added to the oil phase at room temperature while being stirred by means of a high-speed stirrer (disper) to obtain the target W/O emulsified foundation.

Effect)

[0065] The same evaluation as for Examples 1-4 was conducted for the obtained W/O emulsified foundation. The

usability was excellent (usability evaluation: ○). When applied on the skin, it gave moisture, provided a moisturizing sensation and yet was not sticky, and had good stability (stability evaluation: ○).

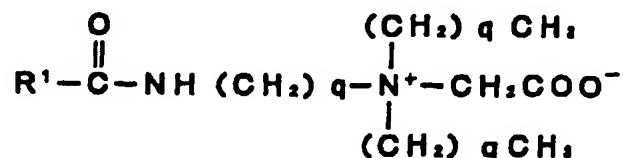
Claims

1. A water-in-oil emulsified cosmetic comprising

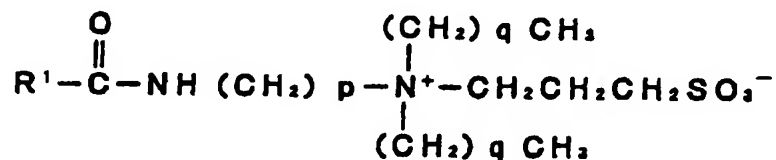
- (A) a complex obtained by mixing an ampholytic surfactant or semi-polar surfactant and higher fatty acid and
(B) an inorganic salt and/or amino acid salt.

2. The water-in-oil emulsified cosmetic of claim 1 wherein said ampholytic surfactant or semi-polar surfactant is one or more surfactants selected from the group consisting of surfactants represented by the following general formulas (1)-(6).

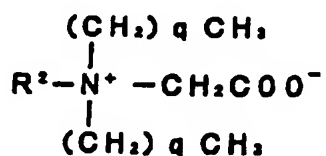
General formula (1): Amide betaine ampholytic surfactants



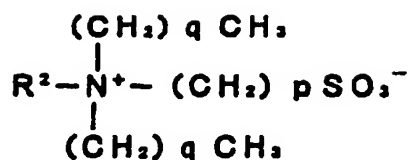
General formula (2): Amide sulfobetaine ampholytic surfactants



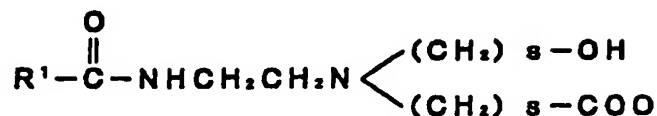
General formula (3): Betaine ampholytic surfactants



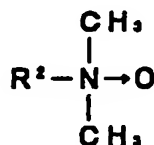
General formula (4): Sulfobetaine ampholytic surfactants



General formula (5): Imidazolinium ampholytic surfactants



General formula (6): Tertiary amine oxide semi-polar surfactants



[In general formulas (1)-(6), R_1 denotes an alkyl or alkenyl group having 9-21 carbon atoms, R_2 and R_3 denote alkyl or alkenyl groups having 10-18 carbon atoms. p denotes an integer 2-4, q denotes an integer 0-3, and s denotes an integer 1 or 2.]

3. The water-in-oil emulsified cosmetic of claim 1 or 2 wherein said higher fatty acid (A) is a higher fatty acid represented by the following general formula (7).



General formula (7)

[Where R_4 denotes a linear chain, branched chain, or hydroxide-group-containing saturated or unsaturated hydrocarbon having 7-25 carbon atoms.]

4. The water-in-oil emulsified cosmetic of claim 1, 2, or 3 wherein the weight ratio of (higher fatty acid) : (ampholytic surfactant or semi-polar surfactant) in said complex (A) is 0.5 : 9.5-9.5 : 0.5.
5. The water-in-oil emulsified cosmetic of claim 1, 2, 3, or 4 wherein said inorganic salt (B) is one or more salts selected from the group consisting of sodium chloride, potassium chloride, magnesium chloride, calcium chloride, aluminum chloride, sodium sulfate, potassium sulfate, magnesium sulfate, and aluminum sulfate.
6. The water-in-oil emulsified cosmetic of claim 1, 2, 3, 4, or 5 of a high inner water phase type wherein the water content is 70.0 wt% or more of the total amount of the water-in-oil emulsified cosmetic.

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SHISEIDO CO LTD

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HONDA SONOKO

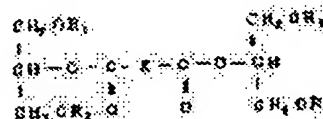
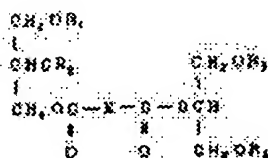
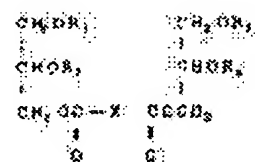
TOMITA KENICHI

(54) COSMETIC

(57)Abstract:

PURPOSE: To prepare cosmetics having excellent color, odor, stability, and applicability, and uniform qualities, by compounding a product having one or more hydroxy groups in a molecule, and obtained by the esterification of glycerine with a $\geq 8\text{C}$ fatty acid (monobasic acid) and a $\geq 12\text{C}$ dibasic acid.

CONSTITUTION: Glycerine is esterified with a monobasic acid comprising a $\geq 8\text{C}$ straight or branched chain saturated and/or hydroxy-fatty acid, e.g. lauric acid, and a $\geq 12\text{C}$ straight or branched chain dibasic acid, e.g. dodecane dicarboxylic acid to obtain a mixed glyceride composed mainly of a compound of formula IWIII (at least one of R1WR4 is H, and the other are acyl derived from the above monobasic acid; X is alkylene derived from the above dibasic acid). The product is suitable as a base of cosmetics because of its high affinity, adhesivity and moistening property to the skin, colorlessness, odorlessness, chemical inactivity, moderate sticking power, high compatibility with wax, solubility in castor oil, drug-dissolving power, etc.



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⑭ 化粧品

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明 細 書

1. 発明の名称
化粧品

2. 特許請求の範囲

1. (1) グリセリン

(2) 炭素数8以上の直鎖脂肪酸、分枝脂肪酸、
不飽和脂肪酸またはヒドロキシ脂肪酸のうち、
1種または2種以上

(3) 炭素数12以上の直鎖または分枝二塩基酸
の上記3成分をエステル化して得られる生成物
のうち、1分子中に1個以上の水酸基を有する
生成物の1種または2種以上を配合することを
特徴とする化粧品。

3. 発明の詳細な説明

本発明は新規な基剤を配合してなる化粧品に関するものであり、色、におい、安定性および使用性に優れ、品質の一定した化粧品を提供することを目的とする。

従来、化粧品に使用されている低融点ワックスの代表的なものとしては、ラノリンおよびワセリンが挙げられる。ラノリンは皮膚に対して親和性、付着性、潤滑性などに富んでおり、また抱水力、乳化力もすぐれているので、基礎化粧品、メークアップ化粧品を始め多くの化粧品に使用されてきたが、色調およびにおいに化粧品原料としての欠点が見られる。また天然物である為品質が一定せず価格の変動も大きく、長時間のうちに劣化する性質などがあるので、近來化粧品に直接使用することは非常に減少している。このためラノリンの構成成分の一部を取り出したり、これに他の物質を反応させ、その特性を残して欠点を少なくした誘導体が化粧品原料として使用されている。しかしこれらの変性を行っても本質的な欠点は依然

2

訂正
訂正
訂正

即ち、本発明は、

(以下余白)

6

(以下余白)

次に、本発明における各原料成分について説明する。

本発明で用いられる一塩基酸の炭素数を8以上と規定したのは、加水分解安定性、皮膚刺激および使用性を考慮したためである。

即ち、炭素数8未満の一塩基酸を用いた場合は加水分解安定性および皮膚刺激が劣り、粘稠性が得られないなどの欠点がある。

炭素数12以上の二塩基酸を用いたのは以下の理由による。

- (1) 生成物の分子量を増大させることによって皮膚刺激を低くさせる。
- (2) 炭素数6以下の二塩基酸を用いた場合、一段階反応で目的の化合物を得ることができない。この場合、グリセリンと一塩基酸と二塩基酸を同時に反応させると、グリセリンと二塩基酸が選択的に反応してビーズ状の重合物を生成する。従って目的の化合物を得るには、グリセリンと一塩基酸のエステルを合成し、未反応のグリセリンを除去してから二塩基酸を反応させなければならない。

ないので少くとも二段階の反応が必要である。

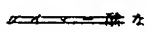
(3) 二塩基酸を用いない時は勿論、二塩基酸を用いた場合でも炭素数が12未満の時はラノリンやワセリンに特有の粘稠性やこしを持たせることができない。

(4) 二塩基酸を使用した場合は、生成物1分子あたりの水酸基の数が多くなるので、エステル化の程度によって極性の変化に幅を持たせることができる。従って処方に合わせて最適な極性の化合物が合成できる。

(5) 二塩基酸の分子量が大きいので、反応温度を高くしても出発原料が揮散しない。

本発明における混合エステルは一般式中の $R_1 \sim R_4$ および X をいろいろ変化させることによって、液体ラノリンから高融点ラノリンやミツロウに到るまでの諸物質に対応するものを調製できる。また、一般式 $R_1 \sim R_4$ のうち少くとも1個を水素としたり、ヒドロキシ脂肪酸を反応させたのは、これによって保湿性を得ることを狙いとしたものである。

本発明における炭素数8以上の直鎖、分枝、不飽和、ヒドロキシ脂肪酸には、ラウリン酸、ミリスチン酸、パルミチン酸、ステアリン酸、ベヘン酸、2-エチルヘキサノ酸、ネオトリデカン酸、イソステアリン酸、オレイン酸、12-ヒドロキシステアリン酸などが該当する。

炭素数12以上の直鎖、分枝二塩基酸には、ドデカン二酸、テトラデカン二酸、ヘキサデカン二酸、オクタデカン二酸、エイコサン二酸、7-エチルオクタデカン二酸、酸などが該当する。

なお、多価アルコール、一塩基酸および二塩基酸から成るエステルに関する公知の技術としては、特公昭51-27447、特開昭51-79731、特開昭52-66637公報記載の技術があげられる。

しかしこれらの公知技術で使用されている二塩基酸は、いずれも炭素数12未満のものであるので、前述の(1)、(2)、(3)、(4)の理由から充分満足のいくものとは言い難い。

本発明における混合エステルは、グリセリンを一塩基酸および二塩基酸で公知の方法でエステル化

して得られる。エステル化には、例えば酸ハライドを利用する方法、エステル基交換法、無触媒および触媒存在下、常圧または減圧下で一塩基酸のグリセリンエステルを合成した後、二塩基酸でエステル化する法、その全く逆の方法およびグリセリン、一塩基酸、二塩基酸を同時に反応させてエステル化する方法等が採用できるが、経済的観点から、グリセリン、一塩基酸および二塩基酸を同時に反応させる方法が望ましい。

(以下余白)

表 - 1

次に本発明における混合エステルの合成例を示す。

合成例 1

攪拌機、温度計、窒素ガス吹込管および水分離器を備えた4つ口フラスコにグリセリン、一塩基酸エステル、二塩基酸とキシレンおよびパラトルエンスルホン酸を全体込量に対してそれぞれ5%、

0.2%を加え、150～250℃にて計算量の水が水分離器にたまるまで反応を行い、反応終了後常法にて脱臭・脱色した。

上記の方法で合成した本発明における混合エステルを表1に示す。

No.	合成に使用した原料 (モル)			主たる成分の構造 (一般式)		融点(℃)	酸価
	アルコール	一塩基酸	二塩基酸	$R_1 \sim R_4$	X		
1	ステアリン酸 モノグリセリド (0.2)	—	ドデカン二酸 (0.1)	2個が $C_{17}H_{35}CO$ 他はH	$(CH_2)_{10}$	52～57	6.1
2	ステアリン酸 モノグリセリド (0.2)	—	エイサン二酸 (0.1)	2個が $C_{17}H_{33}CO$ 他はH	$(CH_2)_8$	64～66	4.1
3	ステアリン酸 モノグリセリド (0.05) イソステアリン酸 モノグリセリド (0.15)	—	エイサン二酸 (0.1)	0.8個が $C_{17}H_{33}CO$ 0.2個が $C_{17}H_{35}CO$ 他はH	$(CH_2)_{10}$	35～49	10.9
4	ステアリン酸 モノグリセリド (0.1) 2-エチルヘキサン酸 モノグリセリド (0.1)	—	ドデカン二酸 (0.1)	1個が $C_{17}H_{35}CO$ 2個が $C_{17}H_{33}CO$ 他はH	$(CH_2)_{10}$	粘稠性の液体	11.5

* ……イソステアリン酸は2-ヘプタリンデカン酸 (三変化成)

(以下余白)

合成例 2

攪拌機、温度計、窒素ガス吹込管および水分離器を備えた4つ口フラスコにグリセリン、一塩基酸、二塩基酸とキシレンおよびパラトルエンスルホン酸を全体込量に対してそれぞれ5%、0.2%を加え、150～250℃にて計算量の水が水分離器にたまるまで反応を行い、反応終了後常法にて脱臭・脱色した。

上記の方法で合成した本発明における混合エステルを表2に示す。

(以下余白)

表 - 2

No.	合成に使用した原料 (モル)			主たる成分の構造 (一般式)		融点(℃)	酸価
	アルコール	一塩基酸	二塩基酸	$R_1 \sim R_4$	X		
1	グリセリン (0.2)	ステアリン酸 (0.2)	ドデカン二酸 (0.1)	2個が $C_{17}H_{35}CO$ 他はH	$(CH_2)_{10}$	20～44	5.5
2	グリセリン (0.2)	ミリスチン酸 (0.1) 12-ヒドロキシ ステアリン酸 (0.1)	ドデカン二酸 (0.1)	1個が $C_{13}H_{27}CO$ 1個が $CH_2(CH_2)_5$ $OH(OH)(CH_2)_9$ CO 他はH	$(CH_2)_{10}$	24～35	10.6
3	グリセリン (0.2)	ステアリン酸 (0.1) イソステアリン 酸 (0.1)	ドデカン二酸 (0.1)	1個が $C_{17}H_{35}CO$ 1.1個が $C_{17}H_{33}CO$ CO 他はH	$(CH_2)_{10}$	20～32	7.2
4	グリセリン (0.2)	イソステアリン 酸 (0.2)	ドデカン二酸 (0.1)	2個が $C_{17}H_{33}CO$ CO 他はH	$(CH_2)_{10}$	粘稠性の液体	7.0
5	グリセリン (0.2)	ベヘン酸 (0.1) イソステアリン 酸 (0.1)	ドデカン二酸 (0.1)	1個が $C_{21}H_{43}CO$ 1個が $C_{17}H_{33}CO$ CO 他はH	$(CH_2)_{10}$	29～49	5.2
6	グリセリン (0.2)	ステアリン酸 (0.1) オレイン酸 (0.1)	テトラデカン 二酸 (0.1)	1個が $C_{17}H_{35}CO$ 1個が $C_{13}H_{27}CO$ 他はH	$(CH_2)_{12}$	33～41	3.7

No.	合成に使用した原料(モル)			主たる成分の構造(一般式)		融点(°C)	濃度
	アルコール	脂肪酸	ニアルコール	R ₁ - R ₂	X		
7	グリセリン (0.2)	イソステアリン酸 (0.12)	エリコサン (0.1)	12個が $C_{15}H_{31}CO$ 他はH	$(CH_2)_{12}$	34~52	12.1
8	グリセリン (0.2)	イソステアリン酸 (0.2)	エリコサン (0.1)	2個が $C_{17}H_{35}$ 他はH	$(CH_2)_{18}$	24~36	6.1
9	グリセリン (0.2)	イソステアリン酸 (0.2)	エリコサン (0.1)	2個が $C_{17}H_{35}$ 他はH	$(CH_2)_{18}$	41~49	3.5
10	グリセリン (0.2)	ラウリン酸 (0.1) ミリスチン酸 (0.1)	7-エチルオ クタデカン二 酸 (0.1)	1個が $C_{11}H_{23}CO$ 1個が $C_{13}H_{27}CO$ 他はH	$(CH_2)_5CH$ $(CH_2CH_2)_2$ $(CH_2)_{10}$	12~21	0.9

※……………イソステアリン酸は2-ヘプテルウンデカン酸
(三酸化成)

※※……………イソステアリン酸はエメリー社製のイソステア
リン酸

次に本発明における混合エステルを配合した化粧料について、実施例により具体的に説明する。

実施例1 クリーム

A部(水相部)

プロピレングリコール	5.0%
精製水	67.7

B部(油相部)

グリセリンエステル(表1の底3)	2.0
ステアリンアルコール	7.0
ステアリン酸	2.0
スクワラン	5.0
2-オクタルドデカノール	6.0
ポリオキシエチレン(25モル)セチルエーテル	3.0
ステアリン酸モノグリセリド	2.0
香料	0.3
防腐剤、酸化防止剤	適量

A部を混合し70℃に保つ。次にB部を混合し加熱融解し70℃に保つ。A部にB部を加えて予備乳化を行ない、ホモミキサーで均一に乳化し、乳化後冷却しながら攪拌する。

このクリームはうるおいのあるしっとりとした

使用感であった。

実施例2 乳液

A部(水相部)

ポリエチレングリコール1500	3.0%
トリエタノールアミン	1.0
精製水	74.5

B部(油相部)

グリセリンエステル(表2の底5)	5.0
ステアリン酸	2.5
セチルアルコール	1.5
流動パラフィン	10.0
ポリオキシエチレン(10モル)モノオレート	2.0
香料	0.5
防腐剤	適量

A部を混合し70℃に保つ。次にB部を混合し、加熱溶解して70℃に保つ。A部にB部を加えて予備乳化を行ない、ホモミキサーで均一に乳化し、乳化後攪拌しながら30℃迄冷却する。

この乳液は皮膚になじみよく、使用感が優れていた。

実施例3 口紅

二酸化チタン	5.0%
赤色204号	0.6
だいだい色203号	1.0
赤色223号	0.2
キャンデリラロウ	9.0
固形パラフィン	8.0
グリセリンエステル(表1の底2)	5.0
グリセリンエステル(表2の底2)	11.0
カルナウバロウ	5.0
ヒマシ油	44.8
イソプロピルミリステート	10.0
香料	適量
酸化防止剤	適量

二酸化チタン、赤色204号、だいだい色203号をヒマシ油の一部に加えローラーで処理する(顔料部)。赤色223号をヒマシ油の一部に溶解する(染料部)。他の成分を混合し加熱融解した後、顔料部、染料部を加えホモミキサーで均一分散する。分散後、現に流し込み冷却する。

この口紅は唇への粘着性がすぐれていた。

実施例 4. リップグロウ

二酸化チタン	0.5 %
赤色 204 号	0.2
オゾケライト	5.0
固形パラフィン	7.0
グリセリンエステル (表 2 の底 4)	50.0
ヒマシ油	27.3
イソプロピルミリスレート	1.0
香料	適量
酸化防止剤	適量

二酸化チタン、赤色 204 号をヒマシ油の一部に加えローラーで処理する (顔料部)。

他の成分を混合し加熱融解した後、顔料部を加えホモミキサーで均一分散する。分散後、型に流し込み冷却する。

このリップグロウは唇に塗布した時、粘着性およびツヤにすぐれていた。

実施例 5. ファウンデーション

カオリン	100 %
二酸化チタン	15.0
亜鉛華	5.0
酸化鉄 (赤)	2.0
酸化鉄 (黄)	4.7
酸化鉄 (黒)	0.3
固形パラフィン	5.0
グリセリンエステル (表 2 の底 8)	15.0
ミリスチン酸オクチルドデシル	8.0
流動パラフィン	30.0
ソルビタンセスキオレート	2.0
香料	適量
防腐剤・酸化防止剤	適量

二酸化チタン、亜鉛華、酸化鉄を混合し粉砕機で処理する (粉末部)。粉末部に流動パラフィンの一部とソルビタンセスキオレートを加えホモミキサーで均一分散し、他の成分を加熱融解して加え容器に充填して 40℃ まで冷却する。

このファウンデーションは付着力が強く、化粧

崩れが少なかった。また防腐剤や酸化防止剤の析出もなかった。

実施例 6. チック

A 部	
グリセリンエステル (表 2 の底 9)	92.0 %
グリセリンエステル (表 2 の底 4)	4.0
酸化防止剤	適量
B 部	
香料	4.0
染料	適量

A 部を混合し加熱溶解する。これに B 部を加え型に流し込み冷却する。

このチックは整髪力が極めて優れていた。

実施例 7. ボマード

A 部	
グリセリンエステル (表 1 の底 1)	20.0 %
ヒマシ油	75.0
酸化防止剤	適量
B 部	
香料	2.0
染料	適量

A 部を混合し加熱溶解する。これに B 部を加え冷却する。

このボマードは整髪力が優れていた。

実施例 8. シャンプー

ラウリルポリオキシエチレン (3 モル) 硫酸ナトリウム (30 % 水溶液)	30.0 %
ラウリル硫酸ナトリウム (30 % 水溶液)	15.0
エチレングリコールモノステアレート	3.0
ラウロイルジエタノールアミド	2.0
グリセリンエステル (表 2 の底 10)	1.0
蛋白質誘導体	3.0
精製水	45.0
香料	適量

染料 適量
防錆剤・紫外線吸収剤・金属イオン封鎖剤 適量
精製水を加熱し、これに他の成分を加えて溶解しよくかきまぜた後ゆっくり冷却する。
このシャンプーはしっとりとした仕上がりであった。

実施例 9 リンス

ステアリルトリメチルアンモニウムクロリド	2.0%
セチルアルコール	2.0
シリコン油	2.0
グリセリンエステル(炭素数18)	1.0
ポリオキシエチレン(10モル)オレイルエーテル	1.0
グリセリン	5.0
蛋白質誘導体	2.0
精製水	85.0
香料	適量
染料	適量
防錆剤・紫外線吸収剤	適量

精製水にグリセリン、蛋白質誘導体、染料を加え加熱溶解して70℃に保つ(水相)。他の成分を

混合し、加熱溶解して70℃に保つ(油相)。油相に水相を加えよくかきまぜる。その後冷却しながら、さらにかきまぜる。

このリンスは毛髪に柔軟性と自然な光沢をあたえた。

特許出願人 株式会社 資 生 堂

手続補正書(自発)

昭和55年9月30日

特許庁長官 島 田 春 樹 殿

1. 事件の表示

昭和54年特許願第094736号

2. 発明の名称

化粧料

3. 補正をする者

事件との関係 特許出願人

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4. 補正の対象

明細書の「発明の詳細な説明」の欄

補正の内容

- (1) 明細書の第3頁第7行目の「溶解しない薬剤」を「溶解しない、薬剤」と補正します。
- (2) 明細書の第3頁第15行目の「適当な」を「適当な」と補正します。
- (3) 明細書の第5頁第2行目の「分枝」を「分枝」と補正します。